Design of a Simple Cryogenic System for Ultraviolet-Visible Absorption Spectroscopy with a Back-reflectance Fiber Optic Probe

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Abstract

We report a convenient and inexpensive technique for the rapid acquisition of absorption spectra from small samples at cryogenic temperatures using a home built cryostat with novel collection optics.

A cylindrical copper block was constructed with a coaxial bore to hold a 4.00 mm diameter EPR tube and mounted on a copper feed in thermal contact with liquid nitrogen. A 6.35 mm diameter hole was bored into the side of the cylinder so a fiber optic cable bundle could be positioned orthogonally to the EPR tube. The light passing through the sample is reflected off of the opposing surfaces of the EPR

tube and surrounding copper, back through the sample. The emergent light is then collected by the fiber optic bundle, and analyzed by a dispersive spectrometer.

Absorption spectra for $KMnO_4$ were measured between 400 nm and 700 nm. Absorption intensity at 506 nm, 525 nm, 545 nm and 567 nm was found to be proportional to concentration, displaying Beer's law like behavior. The EPR tube had an internal diameter of 3.2 mm; the double pass of the probe beam through the sample affords a central path length of about 6.4 mm. Comparing these measurements with those recorded on a conventional tabletop spectrometer using a cuvette with a 10.00 mm path length, we consistently found a ratio between intensities of 0.58 rather than the anticipated 0.64. These 6 % smaller values we attribute to the curvature of the EPR tube and transmission/ reflection losses.

This system is particularly well suited for studying the kinetics and dynamics of chemical reactions at cryogenic temperatures. The rapid response (100 ms) and multiplex advantage provided the opportunity of recording

simultaneous time courses at several wavelengths following initiation of a chemical reaction with a pulsed laser source.

INDEX HEADINGS: Cryostat, UV-Vis spectroscopy, ultraviolet-visible absorbance, fiber optics, reflectance.

Introduction

Over the last several decades, the major emphasis in time resolved spectroscopy has been to measure ever faster chemical events. This has been made possible with the production of shorter light pulses, which have decreased in duration exponentially since the development of flash photolysis by Porter and Norrish in 1949.[1] However, a number of much slower chemical processes are also of significant interest in contemporary chemical physics, in particular, those occurring in super-cooled solutions near the glass transition.[2] Investigations into these longer lived

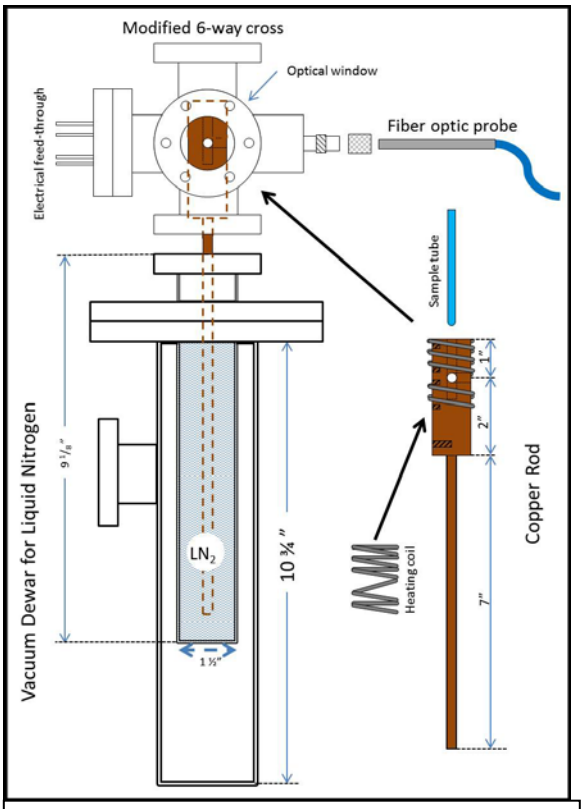

Fig. 1. Cryostat schematic. A vacuum Dewar holds liquid nitrogen. A copper block is in contact with the LN2, and has been bored to accommodate an EPR tube, a fiber optic probe, and a through hole to pass an excitation laser pulse. A heating coil is wrapped around the copper block, and current is manually controlled.

events at cryogenic temperatures are not readily accessible using modern day spectrometers. A number of cryogenic spectroscopic systems have been reported in the literature, and are now even available from commercial sources. These cryogenic spectroscopic systems have been designed to study Ultraviolet-visible[3,4] through Infra-Red absorbance, [5,6] Raman scattering,[7] and fluorescence.[8] However, none are readily convenient to use for the laser pulse initiated, time based absorbance measurements. Likewise, a number of fiber-optic based spectroscopic systems have been developed, and several reviews are available.[9-15] The majority of these rely on two fiber systems, with a sample located between an illumination and a collection fiber, and give true absorbance measurements. An interesting variation on this theme is to use a single fiber and mirrored surface on the opposite side of the sample volume. This method was used by Carroll and Heiftje and Campiglia et al. for low temperature samples,[16,-19] and commercial probes are now available.[20,21] Other fiber optic absorbance probes rely on evanescent wave interactions with the sample,[22,23] or on

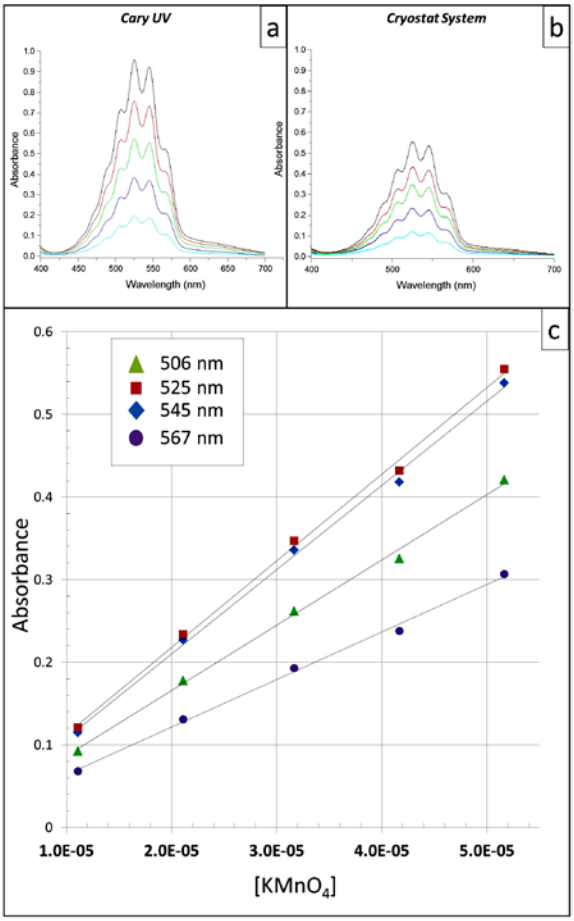

Fig. 2. Comparative spectra and standard curves. Spectra of $KMnO_4$ at various concentrations collected on the a) Cary 100-Bio, and b) cryostat system. c) Plots of absorbance vs. concentration for the cryostat system show good linearity of fit at the four peak wavelengths.

measurement of reflected light.[24-28] The former devices are difficult to calibrate and of low sensitivity, and the later are eminent suitability for opaque sample, but will not work for traditional absorbance measurements.

For the cryogenic spectrometer reported here, the design allows one to measure the transient absorption over a small volume of sample while having a direct knowledge of the temperature in just that limited region. The small volume minimizes unwanted heterogeneity brought about by thermal gradients. A reliably measurable absorption signal is made possible by doubling the path of the probe light through the sample using back reflectance absorption. To the best of our knowledge, this back-reflected absorbance sampling geometry is a serendipitous discovery novel to this instrument.

Experimental

Cryostat Design

An inexpensive cryostat was designed and built using surplus materials; a few commercially available, off-the-shelf components; and a minimum of custom machine work. The estimated materials costs using current price quotes are $1,471 for the essential vacuum components, ~$260 for the sample block and heating parts. Reusable high-precision EPR tubes were used for goodness of fit and UV transmissibility, but at $24 each, compare favorably to a spectrosil cuvette costing $189. Less costly glass NMR tubes could be used, if UV transparency is not relevant. Figure 1 shows a schematic of the cryostat and its components. The cryostat consists of a thermal copper block that has been drilled to accept a sample tube and optics. The copper block is wrapped with heating

wires, and variable current is applied by controlling a rheostat in series with a surplus 200 W computer power supply. A copper rod is attached to the block, which is inserted in a reservoir of liquid nitrogen. The liquid nitrogen is held in a vacuum jacketed Dewar made out of CF flange fitted concentric steel tubing.

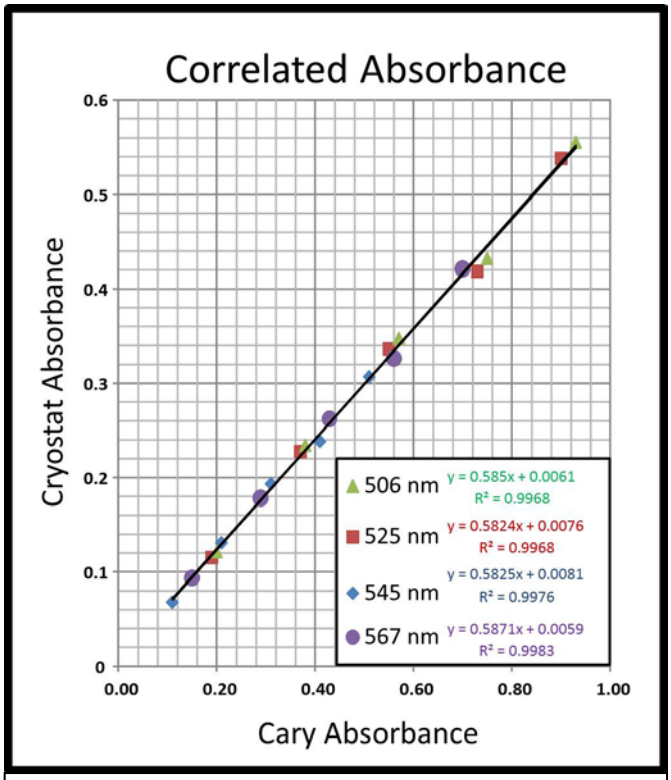

Fig. 3. Cross correlation of spectral responses. The absorbance and concentration data at each wavelength obtained by the Cary 100 is marked on the abscissa. The ordinate data are the absorbance for the corresponding concentration (and wavelength) recorded on the cryostat system. A consistent factor of 0.58 is obtained, and the data are in good agreement with the best fit curve.

The Dewar to hold the liquid nitrogen is of simple design. An outer tube is connected to a small pump (EM-15, Edwards), and a second CF fitted tube is inserted coaxially into the outer tube, forming the inner wall of the Dewar. We note that this design, while simple, is not ideal, and results in a frosting at the junction by the upper CF flanges, and requires re-filling of the LN2 throughout the course of the experiment.

Thermal control of the system was designed with a minimal number of components and cost. A thermal probe (type T thermocouple, Digi-Sense) resides inside the sample itself,

contained within tube. The copper block is in thermal contact with the LN2 via the immersed rod. A 4 foot coil of sheathed tungsten allow wire, (1.2 Ω, 0.015" diameter, %5 Rhenium, Omega Engineering) is connected to the power supply via a standard CF flange wire feed through and wrapped around the copper block near the sample. Careful control of current, and thus heating power, is affected by manual feedback monitoring the applied current and the temperature. A human operator becomes a de facto feedback loop controller, balancing the heating against cooling to maintain a selected temperature.

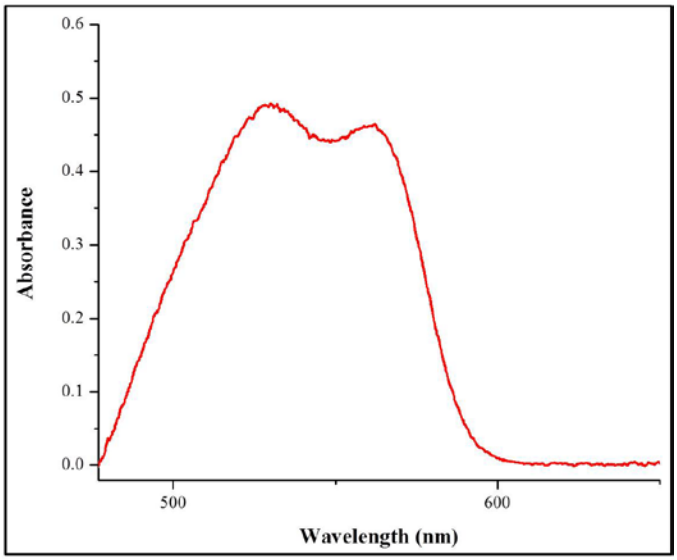

Fig. 4. Spectrum of methyl red dye at low pH and -80 °C.

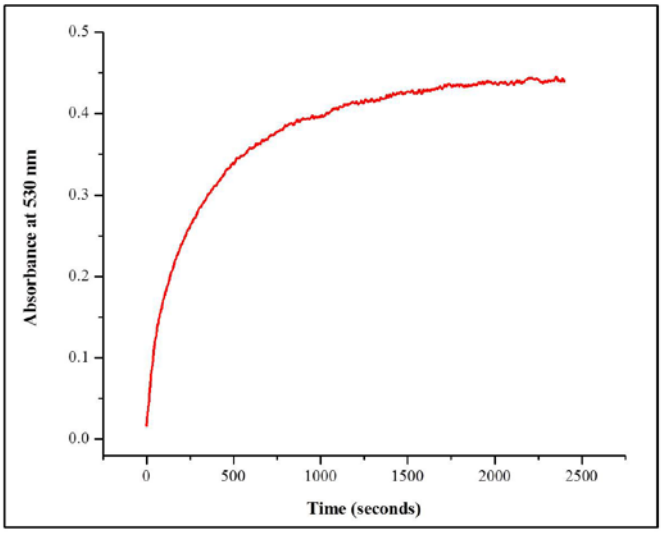

Fig. 5. Plot of absorbance of the peak at 530 nm at vs time at -85 °C. The laser pulse marks t=0, when pH lowers, and the dye converts to its red form.

The optical portion of the spectrometer consists of optical windows, the sample tube, and a fiber-optic probe bundle housed in a modified six-way cross. The copper block and the sample are aligned along the vertical (Z-axis) of the six-way cross. Along the X-axis are

mounted the connections for the electrical feed through and, directly opposing them, the fiber-optic probe. It was necessary to remove the existing CF flange and weld on a Cajon fitting to accommodate the probe. The probe is sold as a reflectance probe (R400-7-UV/VIS, Ocean Optics) and consists of one 400 μm collection fiber surrounded by six emission fibers (400 μm), which are held in a ¼ inch by 3 inch steel ferrule. The probe is fiber optically coupled to a light source (Ocean Optics, LS-1) and a dispersive spectrometer (Ocean Optics, USB 4000). The use of a Cajon-fitted flange would have resulted in the probe tip being too far away from the sample, thus it was necessary to directly weld the Cajon fitting. The probe is inserted through the fitting, into the hole in copper block, and held adjacent to the sample tube. The Y-axis of the cross is in line with the ¼ inch through-hole bored in the copper block. One end of this axis is terminated with CF-Quartz window for pulsed laser excitation of the sample (orthogonal to the probe collection axis), and the other can be fitted to a vacuum pump. The hole is drilled through, to prevent unwanted reflection off the back wall of the copper block, possibly over exciting the sample. Thus, all six faces of the six-way cross are occupied: 1) electrical feed though, 2) collection optics, 3) sample holder, 4) “thermal” feed through, 5) vacuum, and 6) excitation window. There is no possible configuration that will maintain orthogonal laser excitation and conventional in-line absorption geometry. “Doubling up,” e.g. running the electrical feed through and one of the optical paths on the same flange, was deemed impractical and seven-way crosses are not readily available.

Sample Preparation

A stock solution of $KMnO_4$ (Fisher) was prepared by diluting ~3 g of solid in 1 L of water, followed by the addition of 1-2 drops of 12 N HCl (Fisher). Solutions of highly concentrated $KMnO_4$ form strongly scattering colloidal MnO_2 particles. These particles were removed by boiling for 1 h, and stored in the dark overnight. After a minimum of 12 h, the solution was filtered and stored for later use.

For the low temperature kinetics study, a solution was made comprising 3.6×10^{-5} M of the sodium salt of methyl red and 1.3×10^{-3} M nitrobenzaldehyde in 50% glycerol/ water solvent ($\chi_{water} = 0.5$).

Collection of Spectra

Spectra were collected from the same sample on both the cryostat system and a reference conventional scanning UV-Vis (Cary 100-Bio) as close to simultaneously as possible. The stock permanganate solution was diluted until a maximum absorbance of ~1 was recorded on the Cary, and the concentration calculated to be 5.17×10^{-5} M. Subsequent dilutions of this solution by 1 to 4 parts in 5 were made, and the spectrum of each solution was recorded from 400-700 nm on both instruments. The dispersive spectrometer collected 50 scans of 35 milliseconds each which were averaged per spectrum.

For the low-temperature experiments, the methyl red solution was placed in the sample holder, a type T thermocouple inserted carefully into the sample tube, and LN2 added to the dewar. Current was applied to the heating coil, and gradually reduced until the sample reached ~85 °C. The sample was irradiated for two seconds (10 Hz, ~260 mW) with the

third-harmonic from a Q-switched Nd-YAG laser (Continuum, Surelite) was used to lower the pH of the solution. Spectral data were collected as above, and the software monitored the peak at 530 nm over time. Data were collected for 2,500 seconds, and the temperature held at -80 ±1 °C for the duration. A static spectrum of methyl red was collected at -85±1 °C using the same experimental parameters, but not tracked over time.

Data, Results and Discussion

This spectrometer was built to measure both steady state absorption spectra and absorption of transient species. Both of these measurements depend on the extent to which the incident beam is absorbed and therefore on the concentration of the absorbing species in solution. To confirm that this spectrometer follows "Beer's-law-like" behavior, spectra of aqueous solutions at differing concentrations of potassium permanganate were recorded between wavelengths of 400 nm and 700 nm. The use of the permanganate ion has two major benefits (see Figure 2): firstly, the absorption spectrum is highly structured showing six discernable peaks, four of which display local maxima, and secondly, the absorption approaches zero near the ends of the spectral range of interest.

In Figure 2, compares the room temperature spectra measured on the Cary bench top spectrometer (left panel) with those measured on the cryogenic spectrometer (right panel). The curves showing maximum absorption on each instrument represent a stock permanganate ion concentration of 5.17×10^{-5} M, which exhibits an absorbance of close to 1 on the reference spectrometer.

The most noticeable difference between the two sets of spectra is the difference in relative peak heights. Aside from a multiplicative factor, the two set of spectra compare quite favorably. The characteristic spectral features are retained in the data collected on the cryostat system. The cryostat system seems to be more sensitive to the presence of the MnO_2 oxide formation than the Cary. This is most likely due to the cryostat's mechanism of light reflection, wherein the optical path effectively doubles the number of passes through the sample.

Plots of absorbance vs. concentration were constructed for each system at the four peak wavelengths; 567, 545, 525, and 506 nm, and the cryostat is shown in Figure 2c. The data show good linearity of fit for both the conventional UV-Vis, and the new geometry used in the cryostat. As summarized in Table I, the Cary system proved to be an excellent choice for a reference system with little noise, as indicated by the very high R^2 values. The plots obtained from the cryostat data also show good linear concentration response, but also more noise. Several factors could account for some of the variation, including multiplicative scatter noise, the doubling of the path length, the higher susceptibility to colloid scattering, etc.

Although the new cryostat spectrometer shows a linearity of response comparable to that of the reference spectrometer, the absorbance values obtained on the cryostat are approximately 0.6 times those measured from reference spectrometer. To determine if a wavelength dependant response is present, the two data sets were cross-correlated by

plotting the reference absorbance on *x*, and the absorbance from the cryostat on *y* for each concentration and absorbance data pair, as shown in Figure 3. Table II summarizes the cross-correlation data from Figure 3. For each wavelength, the slope of the correlated data was consistent, and the average of the four slopes was 0.5842 (σ = 0.002). This value represents the multiplicative constant that can be used as to convert data acquired on the cryostat to the absorbance values that would be obtained on the well known Cary 100-Bio. Figures 4 and 5 show the results of the low temperature experiments. As expected, the spectrum of methyl red at low temperature (Figure 4), is slightly different than at room temperature, exhibiting a double, rather than single peak. The time course shows the gradual increase in the peak at 530 nm as the methyl red converts to its protonated form, and follows the anticipated shape of a standard kinetic curve. Further analysis of these data will be published later.

Table I. Comparison between the reference spectrometer (Cary 100-Bio) and the cryostat spectrometer of linear least squares data from plots of absorbance *vs.* concentration of $KMnO_4$ at four wavelength maximae. All data show good linear fits. The instrumental response (slope) of the lines is systematically less on the cryostat.

Cary				Cryostat			
λ(nm)	m	b	R^2	λ(nm)	m	b	R^2
506	13475	0.0023	0.9998	506	7907.4	0.0074	0.9972
525	18000	0	1	525	10485	0.0081	0.9976
545	17508	-0.0025	0.9999	545	10199	0.0061	0.9973
567	9835.2	0.0007	0.9999	567	5753.7	0.0065	0.9967

Table II. Cross correlation linear fit data. Data from Fig. 3 show a consistent multiplicative factor between the reference and cryostat systems.

λ(nm)	m	b	R^2
506	0.585	0.0061	0.9968
525	0.5824	0.0076	0.9968
545	0.5825	0.0081	0.9976
567	0.5871	0.0059	0.9983

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